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(71)Applicant : KANEGAFUCHI CHEM IND CO LTD

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(72)Inventor : OKADA YOSHIFUMI
HARA MASAYUKI
NOJIRI HITOSHI

(54) FILMY BONDING MEMBER

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a filmy bonding member excellent in soldering heat resistance, heat resistance and adhesion, in particular capable of bonding at low temperature of $\leq 250^{\circ}\text{C}$.

SOLUTION: This filmy bonding member is such as to be provided with an adhesive layer consisting of a composition essentially comprising (A) 100 pts.wt. of a soluble polyimide and (B) 1-150 pts.wt. of a compound having at least two unsaturated double bonds; wherein it is characterized that, preferably, the T_g of the composition is -20 to 150°C in its B-stage condition, the T_g after cured $70-300^{\circ}\text{C}$, the T_g of the component A is $100-300^{\circ}\text{C}$, and the thermal expansion coefficient after cured is 20-500 ppm.

LEGAL STATUS

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registration]

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CLAIMS

[Claim(s)]

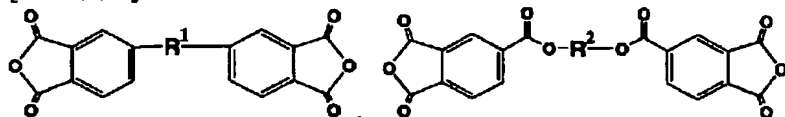
[Claim 1] (A) The film splicing member which comes to prepare the glue line which consists of a constituent which uses as an indispensable component the fusibility polyimide 100 weight section, and the compound 1 - the 150 weight sections which have two or more (B) partial saturation double bonds.

[Claim 2] The film splicing member according to claim 1 characterized by being polyimide with which the aforementioned (A) component is obtained considering acid 2 anhydride which has 1-3 rings, and/or acid 2 alicyclic anhydride as a raw material.

[Claim 3] The film splicing member according to claim 1 or 2 to which the aforementioned (A) component is characterized by being polyimide using the diamine which has the diamine which has 1-5 rings, and/or siloxane association as a 5-100 mol % raw material among [all] diamine.

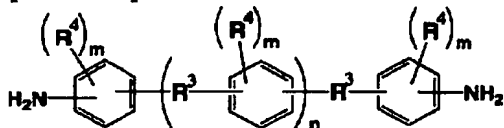
[Claim 4] acid 2 anhydride with which the aforementioned (A) component is chosen from ** 1 — all inside of acid 2 anhydride, 10 - 100-mol % — film bond part material given in any 1 term of claims 1-3 characterized by using. (R1 expresses —, —CO—, —O—, —C(CF3)2—, and —C(CH3)2— among a formula, and R2 expresses a divalent organic radical.)

[Formula 1]



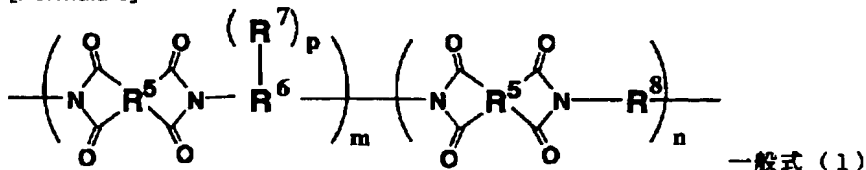
[Claim 5] the diamine as which the aforementioned (A) component is chosen from ** 2 — all inside of diamine, 10 - 100-mol % — film bond part material given in any 1 term of claims 1-4 characterized by using. (the inside of a formula, and R3 - and - in R4, m shows hydrogen, a halogen, a methoxy group, and the alkyl group of C1-C5, and 0, 1, 2, and 3n show 0, 1, 2, 3, and 4 for CO—, —O—, —C(CF3)2—, —C(CH3)2—, and —COO—.)

[Formula 2]



[Claim 6] The aforementioned (A) component is a general formula (1). Film bond part material given in any 1 term of claims 1-5 characterized by what is expressed with-izing 3. (however, the organic radical of tetravalence [inside / of a formula / R5], an organic radical trivalent in R6, an organic radical univalent in R7, an organic radical divalent in R8, and p — the integer of 1-4, and m — one or more integers and n — zero or more integers.)

[Formula 3]



[Claim 7] Film bond part material given in any 1 term of claims 1-6 whose Tg(s) of the aforementioned (A) component are 100 degrees C - 300 degrees C.

[Claim 8] Film bond part material given in any 1 term of claims 1-7 whose aforementioned (B) components are th compounds which hav the acrylic-acid syst m compound which has two or more bitt r taste (meta) roil radicals (meta), the vinyl compound which has two or more vinyl groups, or two allyl groups or mor .

[Claim 9] The film splicing member charact rized by coming to prepare the glue line which consists of a constituent which comes to blend the epoxy resin 1 - th 100 weight sections which have one or more epoxy rings at (C) intramolecular in a constituent given in any 1 term of claims 1-8.

[Claim 10] A film splicing member given in any 1 t rm of claims 1-9 characterized by for Tg after -20 degree-C-150 degree C and hardening being [for Tg of B stage condition of said constituent] 70 degrees C - 300 degrees C, and the coefficient of thermal expansion after hardening being 20 ppm - 500 ppm.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention can carry out adhesion hardening at low temperature comparatively, and relates to the film bond part material excellent in thermal resistance and an adhesive property. The film bond part material of this invention is useful as film bond part material excellent in the thermal resistance used for the tape for a flexible printed circuit board and TAB (Tape Automated bonding), a compound leadframe, the charge of a laminated wood, etc., and an adhesive property.

[0002]

[Description of the Prior Art] In recent years, advanced features of electronic equipment, high-performance-izing, and a miniaturization are progressing, and the miniaturization to the electronic parts used in connection with them and lightweight-ization have been called for. Therefore, high density, high efficiency, and a highly efficient thing have come to be called for more also for the wiring material or wiring components which mount the semiconductor device package approach and them. Especially, printed wired board ingredients, such as high-density-assembly ingredients, such as a semiconductor package, COL and a LOC package, and MCM (Multi ChipModule), and Multilayer FPC, and the ingredient which can be further used suitably as an aerospace ingredient and in which a good adhesive property is shown are called for.

[0003] Conventionally, adhesives, such as acrylic, a phenol system, an epoxy system, and a polyimide system, are known as a semiconductor package or a charge of a binder which shows [in / in addition to this / a mounting ingredient] a good mechanical property, and thermal resistance and insulation.

[0004] However, an adhesive property is inferior to flexibility in them, although the adhesives of a phenol system and an epoxy system are excellent. The problem that thermal resistance is low produces supple acrylic adhesives. Polyimide is used in order to solve this. Since it excels in thermal resistance also in various organic polymers, to space and the aeronautical-navigation field, polyimide is used broadly and used also as film bond part material. However, heat-resistant high polyimide system film bond part material requires the elevated temperature around 300 degrees C, and the high-pressure force, in order to paste up, and it cannot say that adhesive strength is also so high. Moreover, the conventional polyimide system film adhesive had high water absorption, for example, when it was immersed in a solder bath in the leadframe which used this polyimide system film binding material, it had the problem of being easy to produce bulging etc.

[0005]

[Problem(s) to be Solved by the Invention] Then, this invention persons solved the above-mentioned technical problem, were excellent in solder thermal resistance, thermal resistance, and an adhesive property, and as a result of inquiring wholeheartedly for the purpose of offering the film splicing member which can be especially pasted up at low temperature 250 degrees C or less, they came to complete this invention.

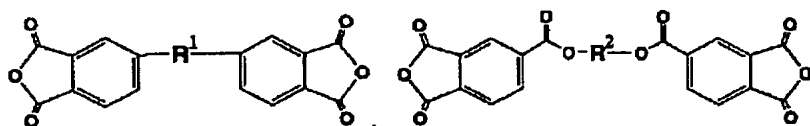
[0006]

[Means for Solving the Problem] this invention persons came to complete a header and this invention for the ability of the predetermined purpose to be attained with a specific adhesives constituent wholeheartedly as a result of examination.

[0007] The first of this invention, the film splicing member which comes to prepare the glue line which consists of a constituent which uses as an indispensable component the (A) fusibility polyimide 100 weight section, and the compound 1 - the 150 weight sections which have two or more (B) partial saturation double bonds The second aforementioned (A) component of this invention the film splicing member according to claim 1 characterized by being polyimide obtained considering acid 2 anhydride which has 1-3 rings, and/or acid 2 alicyclic anhydride as a raw material The diamine in which the third aforementioned (A) component of this invention has the diamine which has 1-5 rings, and/or siloxane association All the inside of diamine, The film splicing member according to claim 1 or 2 characterized by being polyimide used as a 5-100 mol % raw material the fourth of this invention acid 2 anhydride with which the aforementioned (A) component is chosen from ** 4 — all inside of acid 2 anhydride, 10 - 100-mol % — the film bond part material of a publication in any 1 term of claims 1-3 characterized by using (R1 expresses -, -CO-, -O-, -C(CF3)2-, and -C(CH3)2- among a formula, and R2 expresses a divalent organic radical.)

[0008]

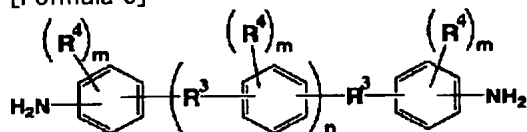
[Formula 4]



The diamine as which the fifth aforementioned (A) component of this invention is chosen from ** 5 All the inside of diamine, 10-100-mol % — a film bond part (R3 among a formula) given in any 1 term of claims 1-4 characterized by using, — in R4, m shows hydrogen, a halogen, a methoxy group, and the alkyl group of C1-C5, and 0, 1, 2, and 3n show 0, 1, 2, 3, and 4 for —CO—, —O—, —C(CF3)2—, —C(CH3)2—, and —COO—.

[0009]

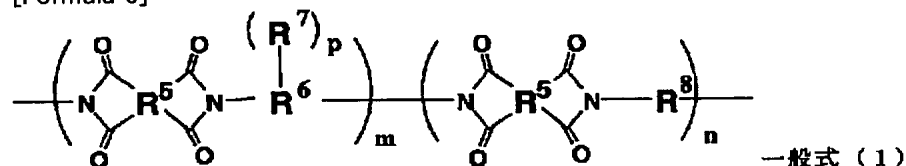
[Formula 5]



The sixth aforementioned (A) component of this invention is a general formula (1). The film bond part material of a publication in any 1 term of claims 1-5 characterized by what is expressed with—izing 6 however, the organic radical of tetravalence [inside / of a formula / R5], an organic radical trivalent in R6, an organic radical univalent in R7, an organic radical divalent in R8, and p — the integer of 1-4, and m — one or more integers and n — zero or more integers —

[0010]

[Formula 6]



The film bond part material of a publication in any 1 term of claims 1-6 whose Tg(s) of the seventh aforementioned (A) component of this invention are 100 degrees C - 300 degrees C the eighth of this invention The acrylic-acid system compound with which the aforementioned (B) component has two or more bitter taste (meta) roil radicals (meta), The film bond part material of a publication in any 1 term of claims 1-7 which are the compounds which have the vinyl compound or two allyl groups or more which have two or more vinyl groups the ninth of this invention The film splicing member characterized by coming to prepare the glue line which consists of a constituent which comes to blend the epoxy resin 1 - the 100 weight sections which have one or more epoxy rings at (C) intramolecular in a constituent given in any 1 term of claims 1-8 Tg of B stage condition of said constituent the tenth of this invention -20 degree-C-150 degree C, Tg after hardening makes the contents a film splicing member given in any 1 term of claims 1-9 characterized by being 70 degrees C - 300 degrees C, and the coefficient of thermal expansion after hardening being 20 ppm - 500 ppm, respectively.

[0011]

[Embodiment of the Invention] (A) The film splicing member which comes to prepare the glue line which consists of a constituent which uses as an indispensable component the fusibility polyimide 100 weight section, and the compound 1 - the 150 weight sections which have two or more (B) partial saturation double bonds, Tg of B stage condition of a constituent preferably -20 degree-C-150 degree C, Tg after hardening is about the film splicing member characterized by being 70 degrees C - 300 degrees C, for Tg of fusibility polyimide being 100 degrees C - 300 degrees C, and the coefficient of thermal expansion after hardening being 20 ppm - 500 ppm. It is detailed and the contents of this invention are explained. The polyamide acid used for this invention is obtained by making it react with the diamine in an organic solvent, and acid 2 anhydride. It adds in the state of the condition of having diffused diamine the dissolution or in the shape of a slurry in the organic solvent in the inert atmosphere of an argon, nitrogen, etc., and having made the organic solvent diffusing acid 2 anhydride the dissolution and in the shape of a slurry, or a solid-state. The diamine of the diamine used by this invention which has a hydroxyl group or a carboxylic acid is used for a kind at least. If diamine [in this case] and acid 2 anhydride is a real good mol, it will become the polyamide acid of one sort of one sort of acid components and diamine components. The mole ratio of these acid 2 anhydride components and a diamine component can be adjusted, and a polyamide acid copolymer can be obtained to arbitration. For example, the diamine component -1 and the diamine component -2 are previously added into the organic polar solvent, subsequently an acid 2 anhydride component is added, and it is good also as a solution of a polyamide acid polymer. Moreover, the diamine component -1 is previously added into the organic polar solvent, an acid 2 anhydride component is added, the after diamine component -2 is added, and it is good also as a solution of a polyamide acid polymer. The diamine component -1 is previously added into the organic polar solvent, subsequently the acid 2 anhydride component -1 is added, subsequently acid 2 anhydride -2 is added, and it is good also as a solution of a polyamide acid polymer. Moreover, the diamine component -1 and the diamine component -2 are previously added into the organic polar solvent, the acid 2 anhydride component -1 is added, subsequently acid

2 anhydride -2 is added, and it is good also as a solution of a polyamide acid polymer.

[0012] The parenchyma top is the same, even if it makes the above-mentioned addition approach revers , it adds acid 2 anhydride previously and it adds a diamine component behind.

[0013] The reaction temperature at this time has -20 degrees C - desirable 90 degrees C. Reaction time is about 24 hours from 30 minutes. As for the average molecular weight of a polyamide acid, it is desirable that it is 5000-1 million. even if the molecular weight of the done polyimide constituent also becomes low and average molecular weight uses the polyimide constituent as it is, it becomes [resin] weak and is not desirable at less than 5000 — it becomes [the viscosity of a polyamide acid varnish becomes high too much, and / handling] difficult and is not desirable if 1 million is exceeded on the other hand.

[0014] Moreover, it is also possible to compound various kinds of organic additives, inorganic fillers, or various kinds of reinforcement with this polyimide constituent. As an organic polar solvent used for the generation reaction of this polyamide acid here For example, sulfoxide system solvents, such as dimethyl sulfoxide and diethyl sulfoxide, Formamide system solvents, such as N,N-dimethylformamide, N, and N-diethyl formamide, Acetamide system solvents, such as N,N-dimethylacetamide, N, and N-diethyl acetamide, Pyrrolidone system solvents, such as a N-methyl-2-pyrrolidone and an N-vinyl-2-pyrrolidone, A phenol, o-, m- or p-cresol, a xylenol, a halogenation phenol, Ether system solvents, such as phenol system solvents, such as a catechol, a tetrahydrofuran, and dioxane, A cellosolve system or hexamethylphosphoramide, such as alcoholic solvent, such as a methanol, ethanol, and a butanol, and butyl cellosolve, Although gamma-butyrolactone etc. can be raised and it is desirable independent or to use these as mixture, aromatic hydrocarbon still like a xylene and toluene is also usable. A solvent will not be limited especially if a polyamide acid is dissolved. Since a polyamide acid is compounded, heating reduced pressure is carried out after that and removal and imide-izing of a solvent are performed to coincidence, it is advantageous on a process to dissolve a polyamide acid and to choose what has the boiling point low if possible. Next, the process which imide-izes a polyamide acid is explained.

[0015] Water is generated in case a polyamide acid imide-izes. This generated water hydrolyzes a polyamide acid easily, and causes the fall of molecular weight. There is the chemical imide-ized method for adding tertiary amine, such as aliphatic series acid 2 anhydrides which usually add azeotropy solvents, such as 1 toluene xylene, and are removed with azeotropy as an approach of imide-izing, such as an approach and two acetic anhydrides, and a triethylamine pyridine picoline isoquinoline, removing this water.

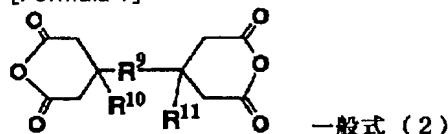
As for removal of the water by the azeotropy of 1), water exists in a solution system, and the hydrolysis by water cannot be avoided. The chemical imide-ized method of 2) is [point / of hydrolysis / the system of 1] advantageous in order that aliphatic series acid 2 anhydride may remove the water to generate chemically by changing to an aliphatic series acid. However, the process at which aliphatic series acid 2 anhydride and tertiary amine remove these for a ***** reason is needed in a system.

[0016] This invention heats and decompresses the water generated by imide-ization, by removing out of a system positively, can suppress hydrolysis and can avoid a molecular weight fall. Moreover, when that one of the two of tetracarboxylic-acid [which carried out ring breakage by hydrolysis], or acid 2 anhydride did [that etc.] adding-water ring breakage mixes into the acid 2 anhydride of the used raw material and the polymerization reaction of a polyamide acid is suspended, it reacts with the amine which acid 2 anhydride which carried out ring breakage carried out the ring closure again, became acid 2 anhydride, and remains in the system during imide-izing with the reduced pressure and heating at the time of imide-izing, and improvement in molecular weight can expect. The heating conditions of imide-izing are 80-400 degrees C. imide — izing — it is carried out efficiently and, moreover, water is removed efficiently — 100 degrees C or more are 120 degrees C or more desirably. as for a maximum temperature, it is desirable to set below to the pyrolysis temperature of the polyimide to be used, and at about 250-350 degrees C, since it completes mostly, imide-ization can boil a maximum temperature to this extent, and can also usually be carried out. Although the conditions of the pressure to decompress have the desirable one where a pressure is smaller, the water which is the above-mentioned heating conditions and is generated at the time of imide-izing should just be the pressure removed efficiently. The pressure which carries out heating under reduced pressure is 0.9 to 0.001 atmospheric pressure, and, specifically, is 0.7 to 0.01 atmospheric pressure still more desirably 0.8 to 0.001 atmospheric pressure desirably. Acid 2 anhydride used for this polyimide constituent Although it will not be limited especially if it is acid 2 anhydride, for example Butane tetracarboxylic dianhydride, 1, 2, 3, 4-cyclobutane tetracarboxylic dianhydride, 1, 3-dimethyl - 1, 2, 3, 4-cyclobutane tetracarboxylic acid, 1, 2, 3, 4-cyclopentane tetracarboxylic dianhydride, 2 and 3, 5-TORIKARUBOKI gardenia fruit clo pentyl acetic-acid 2 anhydride, 3, 5, 6-TORIKARUBOKISHINORUBONAN-2-acetic-acid 2 anhydride, 2, 3 and 4, 5-tetrahydrofuran tetracarboxylic dianhydride, The 5-(2, 5-dioxo tetrahydro FURARU)-3-methyl-3-cyclohexene -1, 2-dicarboxylic acid 2 anhydride, Aliphatic series, such as the bicyclo [2, 2, 2]-oct-7-en -2, 3 and 5, and 6-tetracarboxylic dianhydride, or alicyclic tetracarboxylic dianhydride; Pyromellitic acid, two anhydrides, and 3 and 3 — ' — 4 and 4' - benzophenone tetracarboxylic dianhydride — 3 and 3 — ' — 4 and 4' - biphenyl sulfone tetracarboxylic dianhydride — 1, 4, 5, 8-naphthalene tetracarboxylic dianhydride, 2, 3 and 6, 7-naphthalene tetracarboxylic dianhydride, 3 and 3 — ' — 4 and 4' - biphenyl ether tetracarboxylic dianhydride — 3 and 3 — ' — 4 and 4' - dimethyl diphenyl silane tetracarboxylic dianhydride — 3 and 3 — ' — 4 and 4' - tetraphenylsilane tetracarboxylic dianhydride — 1, 2, 3, 4-furans tetracarboxylic dianhydride, 4, and 4'-screw (3, 4-dicarboxy phenoxy) diphenyl sulfide 2 anhydride, 4 and 4'-screw (3, 4-dicarboxy phenoxy) diphenylsulfone 2 anhydride, 4 and 4'-screw (3, 4-dicarboxy phenoxy) diphenyl propane 2 anhydride, 3, 3', 4, and 4'-perfluoro isopropylidene JIFUTARU acid 2 anhydride, 3, 3', 4, and 4'-biphenyl tetracarboxylic dianhydride, screw (phthalic acid) phenyl phosphine oxide 2 anhydride, p-phenylene-screw (triphenyl

phthalic acid) 2 anhydride, m-phenylene-screw (triphenyl phthalic acid) 2 anhydride, A screw (triphenyl phthalic acid) -4, 4'-diphenyl ether 2 anhydride, a screw (triphenyl phthalic acid) -4 and 4' — aromatic series tetracarboxylic dianhydride; 1, such as - diphenylmethane 2 anhydride, 3,a [3], 4 and 5, 9b-hexahydro -2, and 5-dioxo-3-furanyl-[1 and 2-naphth c] furan - 1 and 3 - dione — 1, 3,a [3], 4, 5, and 9b-hexahydro-5-methyl -5 -(tetrahydro - 2, 5-dioxo-3-furanyl)- The [1 and 2-naphth c] furan -1, 3-dione, 1, 3, 3a, 4, 5, 9b-hexahydro-8-methyl -5 -(tetrahydro - 2, 5-dioxo-3-furanyl)- The [1 and 2-naphth c] furan -1, 3-dione, formation 7 of the following general formula (2)

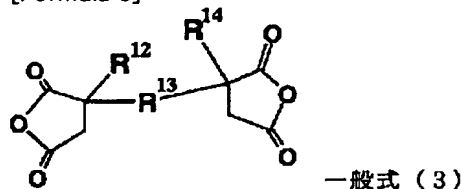
[0017]

[Formula 7]



(As for the inside R⁹ of a formula, the divalent organic radical which has a ring is shown and R¹⁰ and R¹¹ show a hydrogen atom or an alkyl group, respectively.) General-formula[following] (3)-izing 8 [0018]

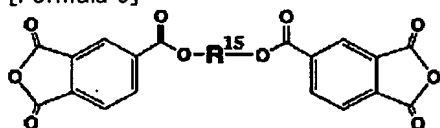
[Formula 8]



(— as for the inside R¹² of a formula, the divalent organic radical which has a ring is shown and R¹³ and R¹⁴ show a hydrogen atom or an alkyl group, respectively.) — the aliphatic series tetracarboxylic dianhydride which has rings, such as a compound expressed, can be mentioned. These tetracarboxylic dianhydride is independent, or can be combined two or more sorts and can be used. In order to obtain the soluble high polyimide to an organic solvent especially, they are 2 and 2'-hexafluoro propylidene JIFUTARU acid 2 anhydride and the following general formula. It is desirable to use a part of ester acid 2 anhydride expressed with-izing 9.

[0019]

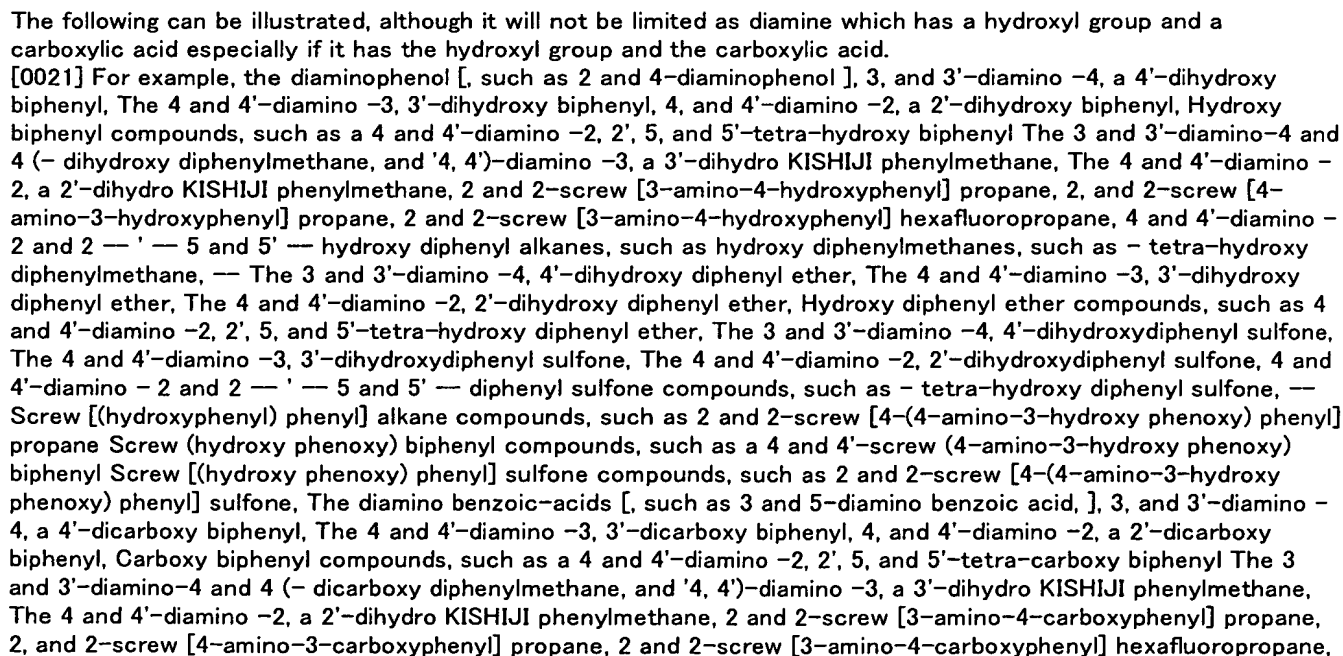
[Formula 9]



(Among a formula, R¹⁵ expresses a divalent organic radical and is 2 and 2-bis-phenyl propylidene still more preferably preferably about the divalent organic radical chosen from ** 10.) R¹⁶ shows a with a carbon number [hydrogen, a halogen methoxy group, and a carbon number] of ten or less alkyl group among a formula.

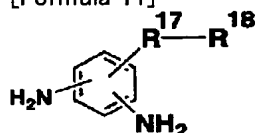
[0020]

[Formula 10]



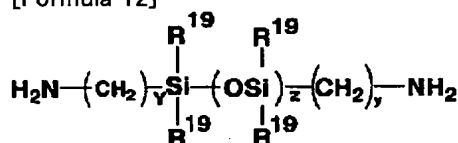
4 and 4'-diamino - 2 and 2' - 5 and 5' - carboxy diphenyl alkanes, such as carboxy diphenylmethanes, such as - tetra-carboxy diphenylmethane, - The 3 and 3'-diamino -4, 4'-dicarboxy diphenyl ether, The 4 and 4'-diamino -3, 3'-dicarboxy diphenyl ether, The 4 and 4'-diamino -2, 2'-dicarboxy diphenyl ether, Carboxy diphenyl ether compounds, such as 4 and 4'-diamino -2, 2', 5, and 5'-tetra-carboxy diphenyl ether, The 3 and 3'-diamino -4, 4'-dicarboxy diphenyl sulfone, The 4 and 4'-diamino -3, 3'-dicarboxy diphenyl sulfone, The 4 and 4'-diamino -2, 2'-dicarboxy diphenyl sulfone, 4 and 4'-diamino - 2 and 2' - 5 and 5' - diphenyl sulfone compounds, such as - tetra-carboxy diphenyl sulfone, - Screw [(carboxyphenyl) phenyl] alkane compounds, such as 2 and 2-screw [4-(4-amino-3-carboxy phenoxy) phenyl] propane Screw (hydroxy phenoxy) biphenyl compounds, such as a 4 and 4'-screw (4-amino-3-hydroxy phenoxy) biphenyl Screw [(carboxy phenoxy) phenyl] sulfone compounds, such as 2 and 2-screw [4-(4-amino-3-carboxy phenoxy) phenyl] sulfone, can be raised. In addition, the diamine used for this polyimide constituent Although it will not be limited especially if it is diamine, for example P-phenylene diamine, m-phenylenediamine, 4 and 4'-(diamino diphenylmethane, and '4, 4')-diamino phenyl ethane, A 4 and 4'-diamino phenyl ether, 4, and 4'-JIJIAMINO phenyl sulfide, 4 and 4'-JIJIAMINO phenyl sulfone, 1, 5-diamino naphthalene, 3 and 3-dimethyl -4, 4'-diamino biphenyl, and 5-amino-1-(4'-aminophenyl)- 1, 3, and 3-trimethyl indan and 6-amino-1-(4'-aminophenyl)- a 1, 3, and 3-trimethyl indan, 4, and 4' - diamino benzanilide A 3 and 5-diamino-3'-trifluoromethyl benzanilide, 3, 4'-diamino diphenyl ether, 2, 7-diamino fluorene, 2 and 2-screw (4-aminophenyl) hexafluoropropane, 4, and 4'-methylenebis (2-chloroaniline), 2, 2', 5 and 5'-tetra-chloro -4, a 4'-diamino biphenyl, 2 and 2'-dichloro -4, the 4'-diamino -5, a 5'-dimethoxy biphenyl, The 3 and 3'-dimethoxy -4, 4'-diamino biphenyl, 4, and 4'-diamino -2, a 2'-screw (trifluoromethyl) biphenyl, 2 and 2-screw [4-(4-amino phenoxy) phenyl] propane, 2 and 2-screw [4-(4-amino phenoxy) phenyl] hexafluoropropane, A 1, 4-screw (4-amino phenoxy) benzene, 4, and 4'-screw (4-amino phenoxy)-biphenyl, 1, 3'-screw (4-amino phenoxy) benzene, 9, and 9-screw (4-aminophenyl) fluorene, A 4 and 4'-(p-phenylene isopropylidene) bis-aniline, 4, and 4'-(m-phenylene isopropylidene) bis-aniline, 2 and 2' screw [-] [4-(4-amino-2-trifluoro methylphenoxy) phenyl] hexafluoropropane, Aromatic series diamines, such as a 4 and 4'-screw [4-(4-amino-2-trifluoromethyl) phenoxy]-octafluoro biphenyl; hetero atoms other than the nitrogen atom of two amino groups combined with rings, such as diamino tetraphenylthiophene, and the amino group concerned Aromatic series diamine which it has; 1 and 1-meta-xylylene diamine, 1,3-propanediamine, A tetramethylenediamine, pentamethylene diamine, octamethylene diamine, Nonamethylene diamine, 4, and 4-diamino heptamethylene diamine, 1, 4-diamino cyclohexane, isophorone diamine, tetrahydro dicyclopentadienylene diamine, Aliphatic series diamine and alicyclic diamines, such as hexahydro -4, 7-methano INDANIREN dimethylene diamine, tricyclo [6, 2, 1, 02.7]-undecylene dimethyldiamine, 4, and 4'-methylenebis (cyclohexylamine);-izing 10 [0022]

[Formula 11]



The mono-permutation phenylenediamines (as for the inside R17 of a formula, the divalent organic radical chosen from -O-, -COO-, -OCO-, -CONH-, and -CO- is shown, and R18 shows the univalent organic radical which has a steroid frame.) come out of and expressed; the following chemical formula -izing 12 [0023]

[Formula 12]



(— R19 shows the hydrocarbon group of carbon numbers 1-12, y is the integer of 1-3, and z is the integer of 1-20.) — the compound expressed can be mentioned. These diamine compounds are independent, or can be combined two or more sorts and can be used. The concrete approach of carrying out stoving of the polyamide acid solution, and forming it into direct imide under reduced pressure, is explained. Although an approach will not be asked under reduced pressure if stoving can be carried out, it can carry out as the approach of vacuum oven and continuous system as the approach of a batch type with biaxial or 3 shaft extruder with which the decompression device accompanied. These methods are chosen by the volume. The equipment from which thermoplastic resin is decompressed to the common melting extruder which performs heating melting extrusion, and a solvent is removed is made to accompany with biaxial or 3 shaft extruder which the decompression device here accompanied. While a polyamide acid solution is kneaded by the extruder with the extruder of biaxial or three shafts, a solvent and the water generated at the time of imide-izing are removed, and it becomes polyimide which has a hydroxyl group or a carboxylic acid. Next, the production process of epoxy denaturation polyimide is explained. The thermoplastic polyimide which has an above-mentioned hydroxyl group or an above-mentioned carboxylic acid is melted to an organic solvent, and epoxy denaturation polyimide is obtained by making it react with the compound which has the epoxy resin and epoxy group which have two or more epoxy groups, double association, or an epoxy group and 3-fold association. The solvent used for a reaction does not react with an epoxy group, and especially if the polyimide which has a hydroxyl group or a carboxylic acid is dissolved, it will not be limited. For example, sulfoxide system

solvents, such as dimethyl sulfoxide and diethyl sulfoxide, Formamide system solvents, such as N,N-dimethylformamide, N, and N-diethyl formamide, Acetamide system solvents, such as N,N-dimethylacetamide, N, and N-diethyl acetamide, Pyrrolidone system solvents, such as a N-methyl-2-pyrrolidone and an N-vinyl-2-pyrrolidone, Ether system solvents, such as a tetrahydrofuran and dioxane, a methanol, Aromatic hydrocarbon still like a xylene and toluene, such as cellosolve systems, such as alcoholic solvent, such as ethanol and a butanol, and butyl cellosolve, or hexamethylphosphoramide, and gamma-butyrolactone, is also usable. These can be used as independent or mixture. A solvent will not be limited especially if the thermoplastic polyimide which has a hydroxyl group or a carboxylic acid is dissolved. Then, since a solvent is removed, it is advantageous on a process to dissolve the thermoplastic polyimide which has a hydroxyl group or a carboxylic acid, and to choose what has the boiling point low if possible. As for reaction temperature, it is desirable to carry out at an epoxy group, a hydroxyl group and a carboxyl group, and the temperature of 40 degrees [130 or less] or more which reacts. About especially the compound that has an epoxy group, two association, or an epoxy group and 3-fold association, it is desirable to make it react at the temperature of extent over which double association and 3-fold association do not decompose or construct a bridge with heat. Specifically, it is 50 degrees [90 or less] or more still more desirably 40 degrees [100 or less] or more. Reaction time is about 8 hours from about several minutes. Although it will not be limited especially if it has two or more epoxy groups in intramolecular, it can be illustrated as the epoxy resin which has two or more epoxy groups as follows.

[0024] For example, bisphenol resin, such as Epicoat 828 (oil-ized shell company make), Orthochromatic cresol novolak resin, such as 180S65 (oil-ized shell company make), Bisphenol A novolak resin, such as 157S70 (oil-ized shell company make), Tris hydroxyphenyl methane novolak resin, such as 1032H60 (oil-ized shell company make), The naphthalene aralkyl novolak resin of ESN375 grade, tetrapod FENI roll ethane 1031S (oil-ized shell company make), YGD414S (Tohto Kasei), tris hydroxyphenyl methane EPPN502H (Nippon Kayaku), Glycidyl amine type resin, such as special bisphenol VG3101L (Mitsui Chemicals), the special naphthol NC 7000 (Nippon Kayaku), TETRAD-X, and TETRAD-C (Mitsubishi Gas Chemical Co., Inc. make), etc. is raised. An epoxy group and the compound which has two association can be illustrated as follows, although it will not be limited especially if it has an epoxy group and double association in intramolecular.

[0025] Allyl-glycidyl-ether glycidyl acrylate glycidyl meta-crate glycidyl vinyl ether etc. can be illustrated. An epoxy group and the compound which has 3-fold association can be illustrated as follows, although it will not be limited especially if it has an epoxy group and 3-fold association in intramolecular. Propargyl glycidyl ether glycidyl PUROPI olate ethynyl glycidyl ether etc. can be illustrated.

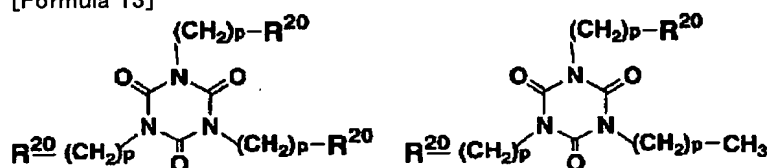
[0026] Thus, the solution of epoxy denaturation polyimide can be obtained. Thermoplastics, such as thermosetting resin, such as an epoxy resin and acrylic resin, and polyester, a polyamide, polyurethane, a polycarbonate, may be suitably mixed with this epoxy denaturation polyimide solution.

[0027] Moreover, since good physical properties are acquired even if it mixes with thermosetting resin other than an epoxy resin, it is this better **. As thermosetting resin used here, bismaleimide bis-ant Luna diimide phenol resin, cyanate resin, etc. are raised. It may direct apply and dry and you may be in the part which joins this epoxy denaturation polyimide solution, and spreading desiccation may be carried out, it may be made the shape of a sheet, and you may be. As for these desiccation conditions, it is desirable to carry out on condition that extent to which an epoxy group, double association, and 3 association which remains does not decompose and construct a bridge with heat. If it usually mixes with the epoxy denaturation polyimide of this invention with the curing agent of an epoxy resin, since the hardened material of good physical properties is obtained, it is desirable. if it is the curing agent of an epoxy resin — an amine system, an imidazole system, an acid-anhydride system, and an acid system — what kind of system may be used. Moreover, various coupling agents may be mixed. Although especially the compound that has two or more partial saturation double bonds of this invention is not limited, its compound which has the acrylic-acid system compound which has two or more bitter taste (meta) roil radicals (meta), the vinyl compound which **** two or more vinyl groups, or two allyl groups or more is desirable, and it can illustrate the following compounds. For example, 1,6-hexanediol diacrylate, neopentyl glycol diacrylate, Ethylene glycol diacrylate, pentaerythritol diacrylate, Trimethylolpropane triacrylate, a pentaerythritol thoria chestnut rate, Dipentaerythritol hexaacrylate, tetramethylolpropanetetraacrylate, Tetraethylene glycol diacrylate, 1, 6-hexanedioldimethacrylate, Neopentyl glycol dimethacrylate, ethylene glycol dimethacrylate, Pentaerythritol dimethacrylate, trimethylolpropanetrimethacrylate, Pentaerythritol trimethacrylate, dipentaerythritol hexamethacrylate, Tetramethylolpropane tetra methacrylate, tetraethylene glycol dimethacrylate, Methoxy diethylene-glycol methacrylate, methoxy polyethylene-glycol methacrylate, beta-METAKUROIUOKISHI ethyl hydrogen phthalate, beta-METAKUROIUOKISHI ethyl hydrogen succinate, A 3-chloro-2-hydroxypropyl meta-crate, a stearyl meta-crate, Phenoxy ethyl acrylate, phenoxy diethylene-glycol acrylate, Phenoxy polyethylene-glycol acrylate, beta-acryloyloxyethyl hydrogen succinate, Laurylacrylate, ethylene glycol dimethacrylate, a diethylene-glycol JIMETA crate, A triethylene glycol JIMETA crate, a polyethylene-glycol JIMETA crate, 1, 3-butylene-glycol JIMETA crate, a 1,6-hexanediol JIMETA crate, A neopentyl glycol JIMETA crate, a polypropylene-glycol JIMETA crate, 2-hydroxy 1, 3 JIMETAKUOKISHI propane, 2, and 2-screw [4-(meta-KUOKISHI ethoxy) phenyl] propane, 2 and 2-screw [4-(meta-KUOKISHI diethoxy) phenyl] propane, 2 and 2-screw [4-(meta-KUOKISHI poly ethoxy) phenyl] propane, A polyethylene-glycol JIKURI rate, tripropylene glycol diacrylate, Polypropylene-glycol diacrylate, 2, and 2-screw [4-(acryloxy diethoxy) phenyl] propane, 2 and 2-screw [4-(acryloxy poly ethoxy) phenyl] propane, A 2-hydroxy 1-acryloxy 3-meta-KUOKISHI propane, trimethylol propane TORIMETAKURETO, Tetramethylolmethane triacrylate, tetramethylolmethane tetraacrylate, A methoxy dipropylene glycol meta-crate, methoxy triethylene glycol acrylate,

Nonyl phenoxy polyethylene-glycol acrylate, nonyl phenoxy polypropylene-glycol acrylate, 1-acryloyloxypropyl-2-phthalate, isostearyl acrylate, Polyoxyethylene-alkyl-ether acrylate, nonyl phenoxy ethylene glycol acrylate, A polypropylene-glycol JIMETA crate, a 1,4-butanediol JIMETA crate, A 3-methyl-1,5-pentanediol JIMETA crate, 1, 6-Mexan diol JIMETA crate, 1, a 9-nonane diol meta-crate, 2, a 4-diethyl-1,5-pentanediol JIMETA crate, 1, 4-cyclohexane dimethanol JIMETA crate, dipropylene glycol diacrylate, Tricyclodecane dimethanol diacrylate, 2, and 2-hydrogenation screw [4-(acryloxy poly ethoxy) phenyl] propane, 2 and 2-screw [4-(acryloxy poly propoxy) phenyl] propane, 2, 4-diethyl-1,5-pentanediol diacrylate, ethoxylation TOCHIMECHIRORU pro pantry acrylate, Propoxy-ized TOCHIMECHIRORU pro pantry acrylate, isocyanuric acid Tori (ethane acrylate), Pen TASURI toll tetraacrylate, ethoxylation pen TASURI toll tetraacrylate, Propoxy-ized pen TASURI toll tetraacrylate, ditrimethylolpropanetetraacrylate, Dipentaerythritol polyacrylate, an isocyanuric acid triaryl, A glycidyl meta-crate, the glycidyl allyl compound ether, 1 and 3, 5-thoria chestnut roil hexahydro-s-triazine, Triaryls 1 and 3, 5-benzene carboxylate, a triaryl amine, a thoria RIRUSHITO rate, triaryl phosphate, allobar BITARU, a diaryl amine, diaryl dimethylsilane, a diallyl disulfide, diaryl ether, a ZARIRU sial rate, JI Allyl compound isophthalate, diaryl terephthalate, 1, 3-JIARIROKISHI-2-propanol, A diaryl sulfide diallyl maleate, 4, and 4'-isopropylidene diphenol JIMETA crate, 4 and 4'-isopropylidene diphenol diacrylate, TORIMESHIKKU acid triaryl ester, A divinylbenzene, divinylbiphenyl, divinyl naphthalene, a divinyl horse mackerel peat, Divinyl ethylene glycol 1, 2-divinyl glycol, divinylmethane 3, 9-divinyl Spirobi (m-dioxane), Divinyl sulfone, 1, 3-divinyl - Although 1, 1, 3, and 3-tetramethyl disilazane, 1, and 3-divinyl tetramethyl siloxane etc. is desirable, it is not limited to these. the compound which has this (meta) acrylic-acid system compound, a vinyl compound, or an allyl group carries out 1-150 weight section combination to the fusibility 100 weight section of this invention — desirable — further — desirable — the 3 - 140 weight section — it is the range of the 20 - 120 weight section most preferably. the effect which is not desirable to physical properties in not acquiring the target effectiveness if it deviates from the range of the 1 - 200 weight section — ***** — there are things. In addition, as a compound which has an acrylic-acid (meta) system compound or two allyl groups or more, one kind of compound may be used, and several sorts may be mixed and used. Especially, the compound which has triazine, isocyanurate, the acrylic-acid system compound that has a SHIANU rate frame (meta), or two allyl groups or more from the point of compatibility with fusibility polyimide is desirable, and, specifically, an isocyanuric acid triaryl, isocyanuric acid diaryl propyl ester, a triaryl SHIANU rate, 1 and 3, 5-thoria KUROIRU-hexahydro-s-triazine, TORIMETA allyl compound isocyanurate, and the compound of ** 13 can be illustrated. (p expresses the integer of 1-10 among a formula, and R20 expresses CH₂=C(CH₃) COO- and CH₂=CHCOO-.)

[0028]

[Formula 13]



The suitable organic solvent may be included in the adhesives constituent used by this invention. If it is in the condition dissolved in the suitable organic solvent, it is convenient, in case use can be presented in the state of a solution (varnish) and a film is produced. Specifically A N-methyl-2-pyrrolidone, an N-acetyl-2-pyrrolidone, An N-benzyl-2-pyrrolidone, N,N-dimethylformamide, N,N-dimethylacetamide, Dimethyl sulfoxide, hexamethylphosphortriamide, N-acetyl-epsilon caprolactam, Dimethyl imidazolidinone, diethylene-glycol wood ether, to which triethylene glycol wood ether, gamma-butyrolactone, dioxane, dioxolane, a tetrahydrofuran, etc. are raised as a suitable example — it is also possible to use these independently and to use as mixed stock. What the solvent used at the synthetic reaction of polyimide could be made to remain as it is, and was newly added to the polyimide precursor after isolation is sufficient as this organic solvent. Moreover, in order to improve spreading nature, even if it mixes solvents, such as toluene, a xylene, a diethyl ketone, methoxybenzene, and cyclopentanone, in the range which does not have a bad influence on the solubility of a polymer, it does not interfere.

[0029] It may direct apply and dry and you may be in the part which joins the solution of this adhesives constituent, and spreading desiccation may be carried out, it may be made the shape of a sheet, and you may be. As for these desiccation conditions, it is desirable to carry out on condition that extent to which the epoxy group and (meta) bitter taste roil radical which remains do not decompose and construct a bridge with heat, and 180 degrees C or less are specifically 150 degrees C or less preferably. C — ** — in case it uses by carrying out, it is made to rival by the pasted up object, a heat lamination and a heat press, or thermal vacuum lamination As for the temperature at this time, it is desirable to carry out at the temperature by which epoxy or double association is not crushed with heat, and 180 degrees C or less are specifically 150 degrees C or less preferably. Moreover, since the adhesive property which may mix the compound which has epoxy groups, such as allyl-glycidyl-ether glycidyl acrylate glycidyl meta-crate glycidyl vinyl ether, and two association other than these is acquired, it is desirable.

[0030]

[Example] Hereafter, although an example explains this invention concretely, this invention is not limited only to these examples.

[0031] the inside of an example, and ESDA — 2 and 2-screw (4-hydroxyphenyl) PUROPANJIBENZOETO — 3 and 3 — ' — 4 and 4' — as for — tetracarboxylic dianhydride and 6FDA, screw [4-(3-amino phenoxy) phenyl] sulfone and DMAc express N,N-dimethylacetamide, and, as for DMF, 2 and 2'-hexafluoro propylidene JIFUTARU acid 2

anhydride and BAPS-M express N and N-dimethyl formamide.

[0032] It measured on conditions below using GPC made from weight-average-molecular-weight Waters. (column: — product [] made from Shodex — part [for /], KD-806M 2 temperature [of 60 degrees C], detector:RI, and flow rate:1ml developing solution:DMF (lithium bromid 0.03M, phosphoric-acid 0.03M), sample concentration:0.2wt%, and injection rate:20microl, and reference-material:polyethylene oxide)

The cast of the measurement ** polyamide acid solution (DMF solution) of the rate of imide-izing is carried out on a PET film, and it removes from a PET film after 100-degree-C 10 minutes and 130-degree-C 10-minute heating, and fixes to a pin frame, and 250 degrees C is heated for 60 minutes for 200-degree C 60 minutes, and 150 degrees C of 5-micrometer thickness polyimide films are obtained for 60 minutes. ** The polyimide created in the example or the example of a comparison was melted to DMF, the cast was carried out on the PET film, and it removed from the PET film after 100-degree-C 30-minute heating, and fixed to the pin frame, and in vacuum oven, stoving was carried out on condition that 80-degree-C5mmHg for 12 hours, and the polyimide film of 5-micrometer thickness was obtained. IR of each film is measured and it asks for the ratio of absorption of absorption/benzene ring of imide. ** Ask for to what% the ratio of the absorption/benzene ring of the imide of ** when making the ratio of absorption/benzene ring of the obtained imide into 100% of rates of imide-izing corresponds. Let this be a rate of imide-izing.

[0033] The solution of the measuring method adhesives constituent of bond strength is applied to a polyimide film (Kaneka APIKARU 25 NPI), 80 degrees C dries for 120-degree-C 5 minutes for 30 minutes for 60-degree C 5 minutes, and 45 degrees C of laminating sheets of polyimide / adhesives constituent are obtained for 5 minutes. The adhesives constituent and copper foil (Mitsui Mining & Smelting electrolytic-copper-foil 3EC- VLP) of this laminating sheet were doubled, it laminated by cm in 120 degrees C and 1kg a pile /, and the layered product of polyimide / adhesives constituent / copper foil was obtained. this — 100-degree-C 1 hour, and 120-degree-C 1 hour, and 140-degree-C 1 hour — 170-degree C 160 degrees C were heated for 3 hours for 1 hour. This layered product was measured according to JIS-6472-1955.

[0034] Tg measuring method profit **** fusibility polyimide solution of fusibility polyimide — a PET film top — applying — 50-degree-C 5 minutes — 90 degrees C dries for 5 minutes, and 70 degrees C exfoliates from a PET film for 5 minutes. This film was fixed by the pin frame, it heated in vacuum oven at 80 degrees C for 12 hours, and the film of fusibility polyimide was obtained. This is measured in thermal-analysis equipment TMA[by SEIKO electronic industry incorporated company]-120C, and temperature of the strange pole is set to Tg of fusibility polyimide.

[0035] Spreading desiccation of the solution of Tg measuring method adhesives constituent of B stage condition is carried out on PET, and it considers as the shape of a film. This was removed, it measured with the thermal-analysis equipment DSC220 by SEIKO electronic industry incorporated company, and Tg was obtained.

[0036] It applies on Tg after hardening, and the measuring method aluminum foil of the coefficient of thermal expansion after hardening, and it dries for 90-degree-C 5 minutes, and to 100-170 degrees C, by part for about 10-degree-C/, a temperature up is carried out and 50-degree C 170-degree C 70 degrees C are heated for 2 hours for 5 minutes for 5 minutes. Aluminum foil is etched and removed and the film of a hardened material is obtained. This film is measured in thermal-analysis equipment TMA[by SEIKO electronic industry incorporated company]-120C, and let it be Tg after hardening the temperature of the strange pole, and a coefficient of thermal expansion after hardening a 30 degrees C - 100 degrees C average coefficient of thermal expansion.

[0037] Temperature from which the ***** film obtained by Tg measuring method after measuring method hardening of heat weight reduction initiation temperature was measured in air by thermal-analysis equipment TG/DTA220 by SEIKO electronic industry incorporated company, and weight reduction became 5% about heat weight reduction is made into heat weight reduction initiation temperature.

[0038]

[Example 1] BAPS-M43.05g (0.1 mols) and DMF300g were taken to the 2000ml separable flask which installed the agitator, and in addition, stirring was continued for 30 minutes as it is, stirring ESDA115.3g (0.20 mols) violently at a stretch. Subsequently, 15.2g (0.1 mols) of diamino benzoic acids was melted to DMF150g, in addition to the above-mentioned solution, it stirred for 30 minutes and the polyamide acid solution was obtained. The weight average molecular weight (it expresses Mw henceforth) of this polyamide acid was 60,000.

[0039] Heating under reduced pressure of this polyamide acid solution was carried out in vacuum oven for the bat which carried out the Teflon (trademark) coat by the pressure of 10-minute and 160-degree-C10-minute and 170-degree-C10 minutes, and 150-degree-C30 minutes and 5mmHg per minute. [180 degree-C] [190 degree-C10 210 degree-C] [10 minutes, and] It took out from vacuum oven and the thermoplastic polyimide which has a 160g carboxylic acid was obtained. Mw of this polyimide was [190 degrees C and the rate of imide-izing of 65,000 and Tg] 100%.

(Fusibility polyimide: Composition of epoxy denaturation polyimide) Compound thermoplastic polyimide 33g is dissolved in dioxolane 66g, and it is epoxy by the oil-ized shell company. 828 3g was dissolved and added to dioxolane 25g. Heating stirring was performed at 70 degrees C for 2 hours, and epoxy denaturation polyimide was compounded. In 100g of epoxy denaturation polyimide solutions, 4 and 4'-diamino diphenyl sulfone (: henceforth abbreviated to DDS curing agent of epoxy group content compound) 0.5g, Iso SHINURU acid Tori (ethane acrylate) 30g, epoxy 828 by the oil-ized shell company 3g, Par hexa by Nippon Oil & Fats Co., Ltd. 25B (polymerization initiator of the compound which has a partial saturation double bond) It is the Kaneka polyimide film about the solution which added 1.5 g. It applies to APIKARU NPI (25-micrometer thickness). 45 degrees C dried for 5 minutes,

the pet film was removed, it fixed by the pin frame, 80 degrees C dried for 30 minutes for 65-degree C 5 minutes, and APIKARU NPI / film splicing member (thickness of 20 micrometers) was obtained. It laminated on 120 degrees C (Mitsui Mining & Smelting VLP electrolytic copper foil) of copper foil, and 1kg pile [/cm] conditions. After the lamination, it hardened on 100-degree-C 2-hour and 120-degree-C 2 hours, and with an hours [2 hours] of 140 degrees C 170-degree-C conditions of 3 hours, and the flexible copper-clad plate (layered product) was obtained. The coefficient of thermal expansion after 25 degrees C, Tg230 degree C after hardening of a constituent, and hardening of a constituent of 1.5kg the pile [cm] /and the solder heatproof was [58 ppm and the heat weight initiation temperature of a constituent / the bond strength of 300 degrees C or more and this flexible copper-clad plate] good [Tg of Tg195 degree C of epoxy denaturation polyimide, and B stage]. Although dipped in the NMP solution which carried out etching removal of the copper foil of a flexible copper-clad plate, and heated the constituent after hardening which remained at 50 degrees C for 10 minutes, it did not dissolve at all.

[0040]

[Example 2] Thermoplastic polyimide 33g which has the carboxylic acid compounded in the example 1 is dissolved in dioxolane 66g, glycidyl methacrylic ester 1.4g (12 millimol) is dissolved and added to dioxolane 10g there, and they are after heating stirring and Asahi Denka Kogyo epoxy for 30 minutes at 60 degrees C. ADEKAOPUTOMA KRM-2110 Heating stirring was performed for 60 minutes at 60 degrees C after adding 3.4g (12 millimol), and epoxy denaturation polyimide was compounded. It is 4 and 4'-diamino diphenyl sulfone (it abbreviates to DDS henceforth) 0.5g, and par hexa by Nippon Oil & Fats Co., Ltd. 25B in 100g of epoxy denaturation polyimide solutions. The solution which added 1.5g and iso SHINURU acid Tori (ethane acrylate) 30g was film-ized on the same conditions as an example 1, and the flexible copper-clad plate was produced.

[0041] Tg of epoxy denaturation polyimide — 1.4kg the pile [cm] /and the solder heatproof were [the coefficient of thermal expansion after 200 degrees C and hardening of a constituent / 70 ppm and the heat weight initiation temperature of a constituent / the bond strength of 300 degrees C or more and this flexible copper-clad plate] good [Tg of 195 degrees C and B stage / Tg after 20 degrees C and hardening of a constituent]. Although dipped in the NMP solution which carried out etching removal of the copper foil of a flexible copper-clad plate, and heated the constituent after hardening which remained at 50 degrees C for 10 minutes, it did not dissolve at all.

[0042]

[Example 3] BAPS-M68.88g (0.16 mols) and DMF300g were taken to the 2000ml separable flask which installed the agitator, and in addition, stirring was continued for 30 minutes as it is, stirring ESDA115.3g (0.20 mols) violently at a stretch. subsequently, 3 and 3'-dihydroxy -4 and 4' - diamino biphenyl 4.32g (0.02 mols) — in addition, for 30 minutes — stirring — subsequently — the product made from silicon diamine PCR — 66M13 26g (0.02 mols) — in addition, it stirred for 30 minutes and the polyamide acid solution was obtained. The weight average molecular weight (it expresses Mw henceforth) of this polyamide acid was 58,000. Under the present circumstances, it reacted by cooling by iced water.

[0043] Heating under reduced pressure of this polyamide acid solution was carried out in vacuum oven for the bat which carried out the Teflon coat by the pressure of 10-minute and 160-degree-C10-minute and 170-degree-C10 minutes, and 150-degree-C30 minutes and 5mmHg per minute. [180 degree-C] [190 degree-C10 210 degree-C] [10 minutes, and] It took out from vacuum oven and the thermoplastic polyimide which has a 202g hydroxyl group was obtained. Mw of this polyimide was [190 degrees C and the rate of imide-izing of 62,000 and Tg] 100%.

(Composition of epoxy denaturation polyimide) Compound thermoplastic polyimide 33g was dissolved in dioxolane 66g, and triethylamine 0.5g and glycidyl methacrylate 1.0g (7 millimol) were dissolved and added to dioxolane 25g there. Heating stirring was performed at 60 degrees C for 2 hours, and epoxy denaturation polyimide was compounded. 100g of epoxy denaturation polyimide solutions — DDS0.5g, isocyanuric acid Tori (ethane acrylate) 30g, and oil-ized shell company make — epoxy 1032H60 The solution which added 3g and par butyl IF by Nippon Oil & Fats Co., Ltd. 1.5g was applied on Kaneka APIKARU NPI (25-micrometer thickness), and APIKARU NPI / film splicing member (20-micrometer thickness) was obtained like the example 1. Moreover, the flexible copper-clad plate was obtained like the example 1. Tg of epoxy denaturation polyimide — 1.2kg the pile [cm] /and the solder heatproof were [the coefficient of thermal expansion after 245 degrees C and hardening of a constituent / 65 ppm and the heat weight initiation temperature of a constituent / the bond strength of 300 degrees C or more and this flexible copper-clad plate] good [Tg of 200 degrees C and B stage / Tg after 40 degrees C and hardening of a constituent]. Although dipped in the NMP solution which carried out etching removal of the copper foil of a flexible copper-clad plate, and heated the adhesives constituent after hardening which remained at 50 degrees C for 10 minutes, it did not dissolve at all.

[0044]

[Example 4] It is 4 and 4'-diamino diphenylmethane in 100g of epoxy denaturation polyimide solutions compounded in the example 1. 0.5g, Iso SHINURU acid Tori (ethane acrylate) 15g, divinylbenzene 15g, Epoxy 828 by the oil-ized shell company It is the Kaneka polyimide film about the solution which added 3g and the 25B1.5 g par hexa by Nippon Oil & Fats Co., Ltd. It applies to APIKARU NPI (25-micrometer thickness). 45 degrees C dried for 5 minutes, the pet film was removed, it fixed by the pin frame, 80 degrees C dried for 30 minutes for 65-degree C 5 minutes, and APIKARU NPI / film splicing member (thickness of 20 micrometers) was obtained.

[0045] The coefficient of thermal expansion after 25 degrees C, Tg220 degree C after hardening of a constituent, and hardening of a constituent of 1.4kg the pile [cm] /and the solder heatproof was [65 ppm and the heat weight initiation temperature of a constituent / the bond strength of 300 degrees C or more and this flexible copper-clad plate] good [Tg of Tg195 degree C of epoxy denaturation polyimide, and B stage]. Although dipped in the NMP

solution which carried out etching removal of the copper foil of a flexible copper-clad plate, and heated the constituent after hardening which remained at 50 degrees C for 10 minutes, it did not dissolve at all.

[0046]

[The example 1 of a comparison] The plater bond M1276 (copolyamide, the Japanese Lil Sun Co., Inc. make) was dissolved in 20g, and 4, 4'-diamino diphenyl sulfone 3g was dissolved for Epicoat 1032H60 in 83g DMF. The obtained varnish was cast on the polyimide film (APIKARU 25AH, Kaneka Co., Ltd. make), it dried at 150 degrees C after desiccation for 10 minutes by 100 degrees C for 10 minutes, and film-like joint material with a thickness of 30 micrometers was obtained. The obtained film-like joint material was put by the polyimide film (APIKARU 50AH, Kaneka Co., Ltd. make) and 25-micrometer copper foil, heating pressurization was carried out by the temperature of 200 degrees C, and pressure 3MPa for 20 minutes, and the copper-clad flexible laminate was obtained.

[0047] When the heat weight initiation temperature of a constituent to which 110 degrees C was not able to measure T_g after 30 degrees C and hardening of a constituent, and, as for T_g of B stage, a constituent was not able to measure the coefficient of thermal expansion easily soaked the bond strength of 230 degrees C and this flexible copper-clad plate in 0.8kg the pile [cm] /and the solder bath, bulging produced it. Swelling degradation was carried out when dipped in the NMP solution which carried out etching removal of the copper foil of a flexible copper-clad plate, and heated the constituent after hardening which remained at 50 degrees C for 10 minutes.

[0048]

[Effect of the Invention] Thus, it excels in solder thermal resistance, thermal resistance, and an adhesive property, and the adhesives constituent which can be especially pasted up at low temperature 250 degrees C or less can be offered.

[Translation done.]